

CLEERS Passive NO_x Adsorber (PNA)

**János Szanyi, Konstantin Khivantsev,
Libor Kovarik, Yong Wang**

Pacific Northwest National Laboratory

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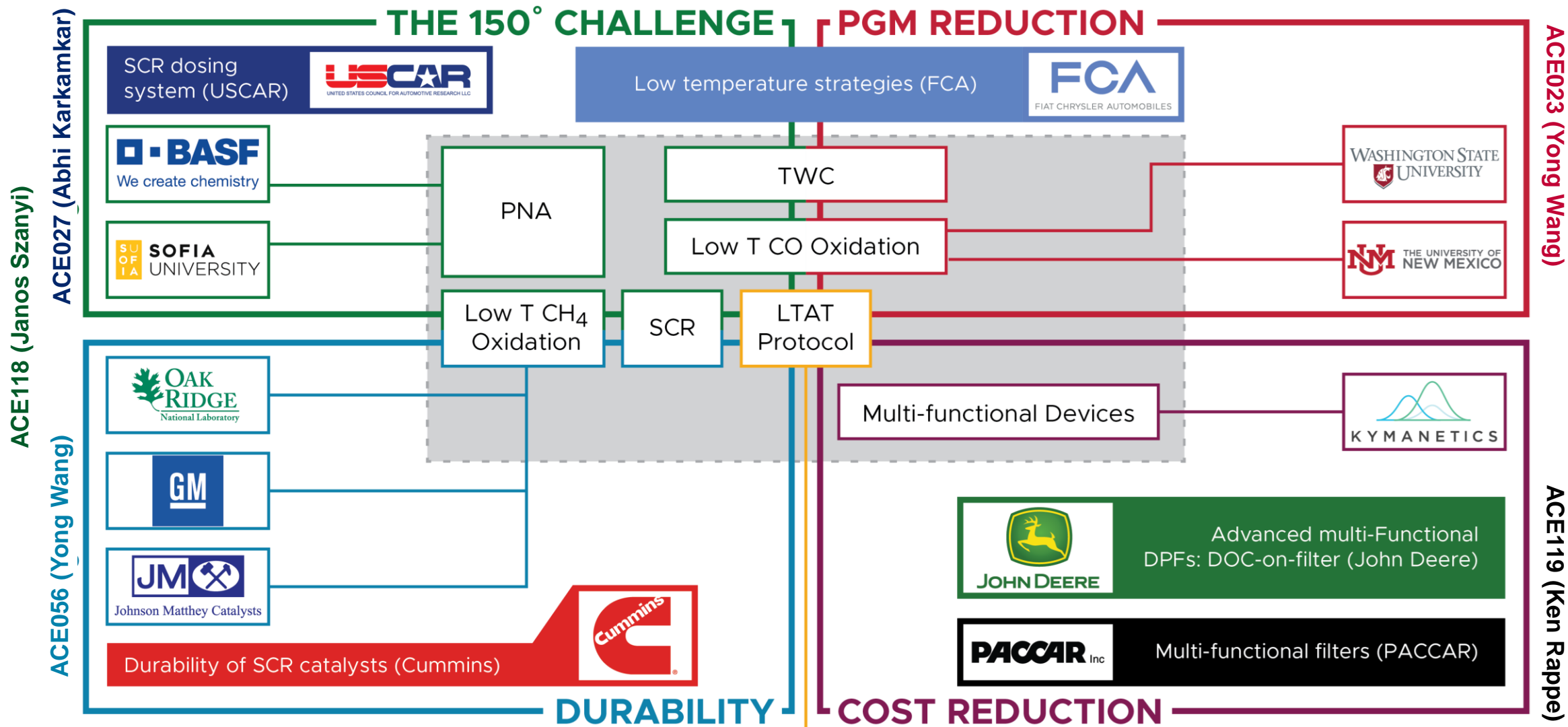
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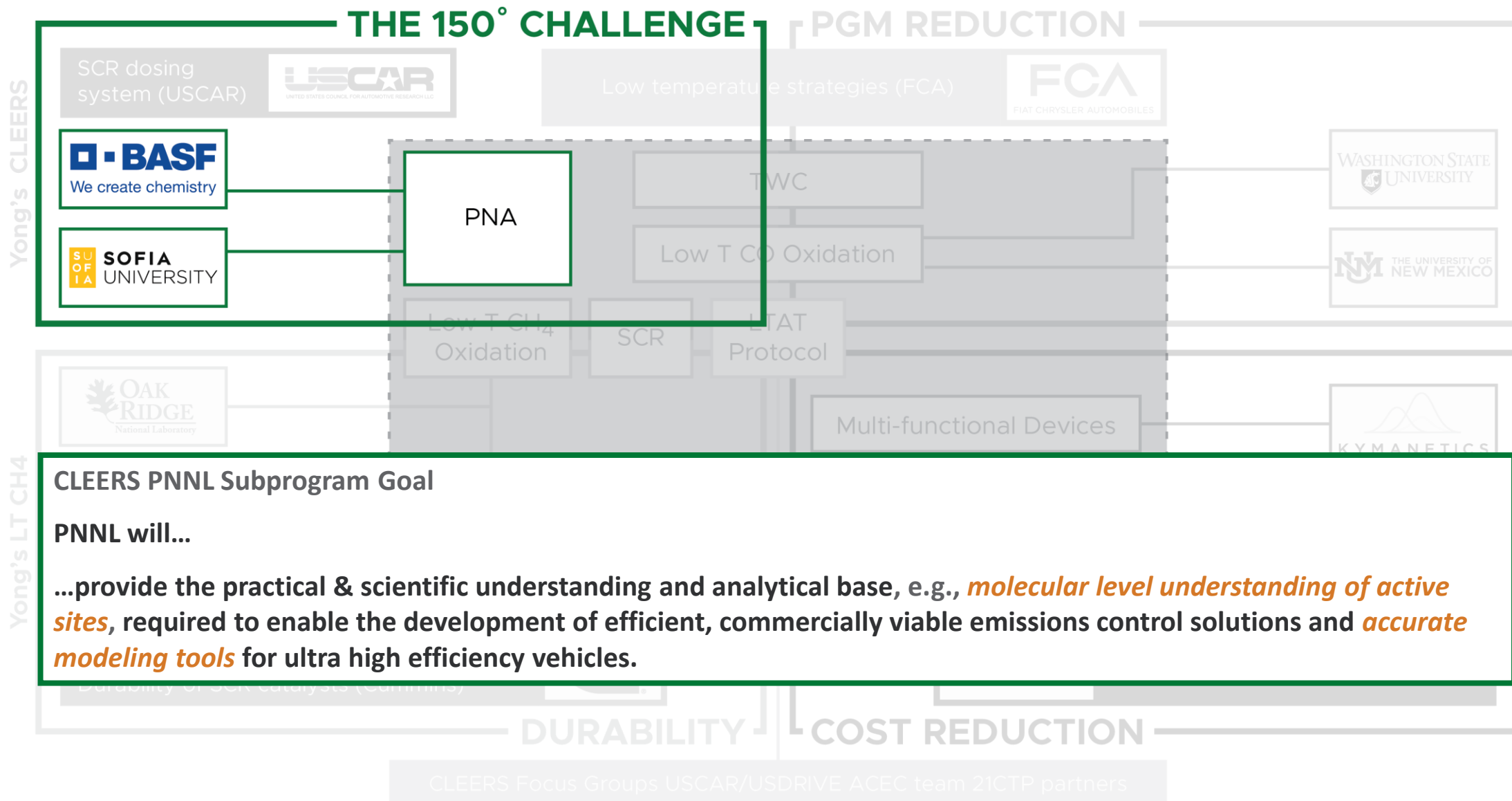
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PNNL Fundamental and CRADA Projects Address the 150°C Challenge, PGM Reduction, Durability, and Cost - Exemplified by 5 AMR Presentations

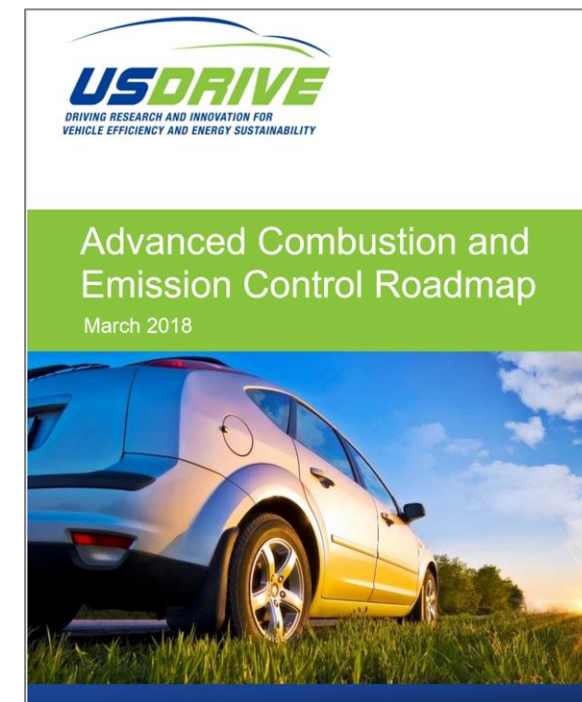


PNA Project Specifically Addresses the “150 °C Challenge” through Fundamental Studies of the Active Sites



Relevance

- ▶ Increasing the efficiency of internal combustion engines
 - dramatically **improves the fuel economy** of the nation's fleet of vehicles
 - **reduces** our **dependence on foreign oil and reducing carbon emissions**.
- ▶ The overarching **emissions goal** is the U.S. EPA Tier 3 Bin 30 emission standard.
- ▶ Aftertreatment technologies are required to be **integrated with the engine combustion** approaches.
- ▶ **Achieve greater than 90% conversion of criteria pollutants** (NO_x , CO, HCs) at **150°C** for the full useful life of the vehicle (defined as the longer of 150,000 miles or 15 years).
- ▶ Require the research and **development of new and novel material combinations** that will enable lower temperature catalytic performance, increased selectivity to inert species, and **optimal storage of pollutant** and reductant species.



Overview



Timeline

- ▶ Status: On-going core R&D

Budget

- ▶ FY19 funding – \$400K

Barriers and Technical Targets

- ▶ Emission controls contribute to durability, cost and fuel penalties
 - Low-temp performance is now of particular concern
- ▶ Improvements limited by:
 - Available modeling tools
 - Chemistry fundamentals
 - Knowledge of material behavior
- ▶ Effective dissemination of information

Partners

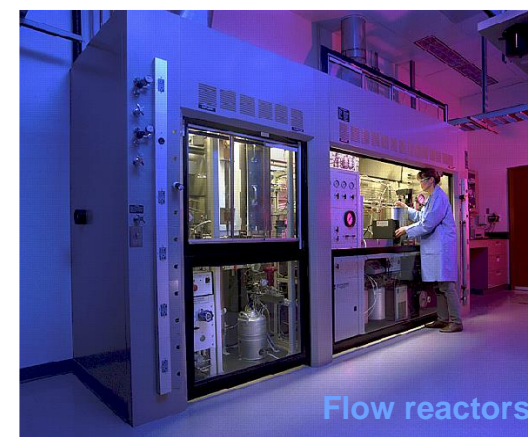
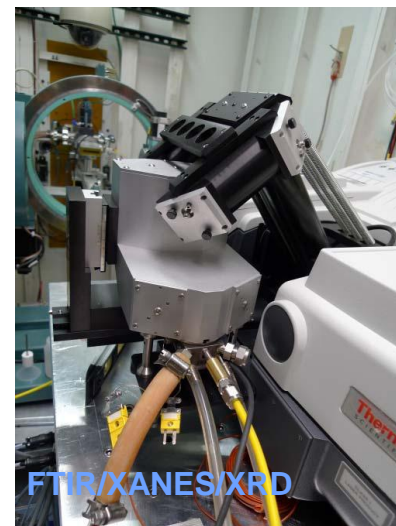
- ▶ Oak Ridge National Lab: synergies in evaluating both practical and model materials
- ▶ BASF: focus on addressing industrially relevant issues

Milestones

	Milestone Description	Date	Status
Go/No-Go	Demonstrate >95% NO _x adsorption within 3 mins at 100 °C and release at >200 °C	9/30/2019	√
Milestone	Report on PNA hydrothermal stability and sulfur tolerance	9/30/2019	√
Milestone	Identify the major cause of PNA material degradation associated with hydrothermal aging and cycling	12/31/2019	√
Milestone	Zeolite supported Pd may be interfered by the presence of HCs	09/30/2020	On track

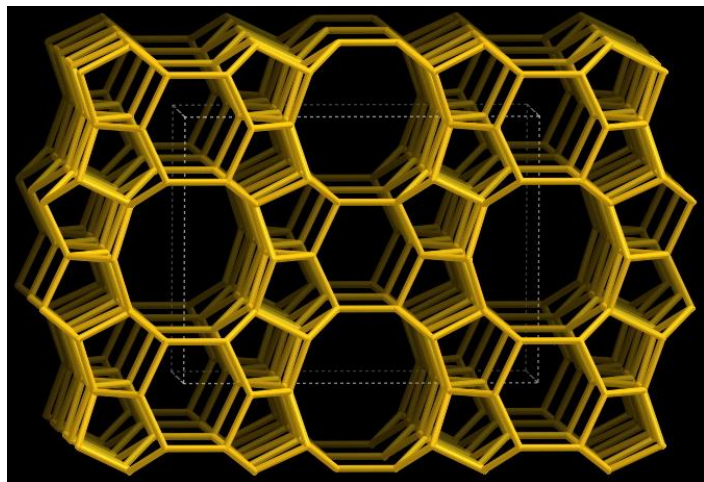
“Science to Solutions”

- ❑ Build on our strong base in fundamental sciences to reveal fundamental aspects of the chemistry and catalytic materials in PNA:
 - ✓ Institute for Integrated Catalysis (IIC)
 - ✓ Environmental Molecular Sciences Laboratory (EMSL)
 - ✓ Synchrotron Facilities
- ❑ Work closely with our partners and sponsors
 - ✓ ORNL (synergy in PNA, etc.)
 - ✓ BASF (addressing the issues of most importance to industry)

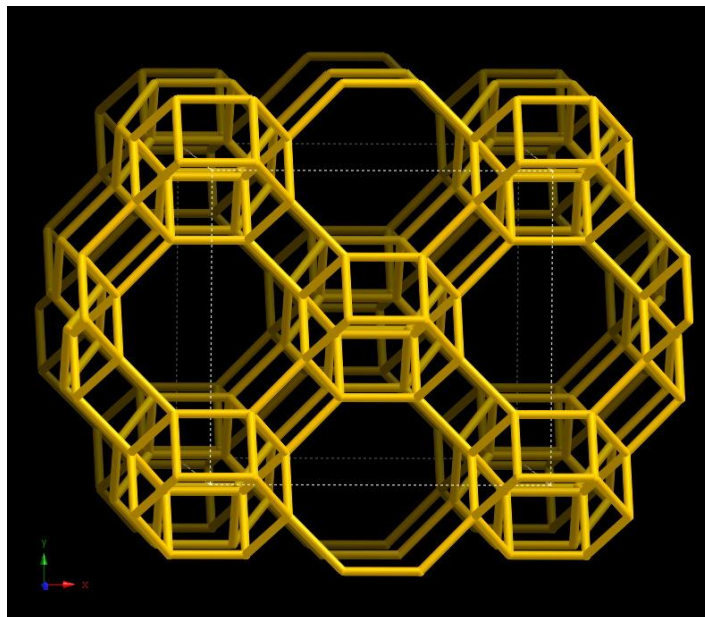


Focus on: Hydrothermally Stable Small Pore Zeolites *and* Performance under Extreme Conditions

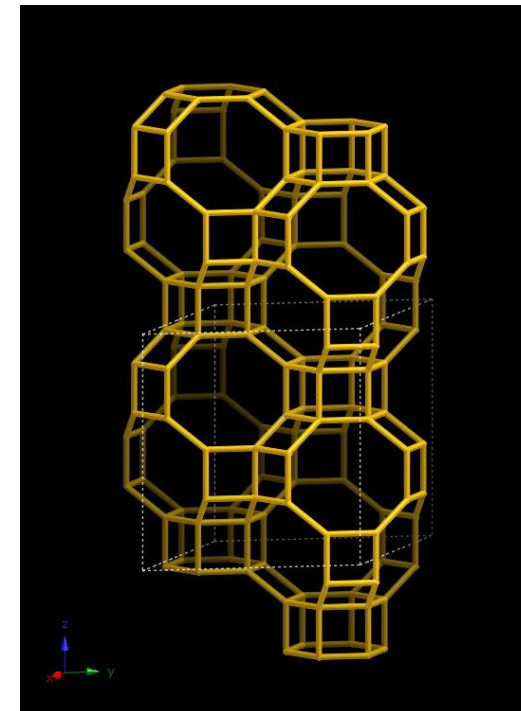
FER



SSZ-39

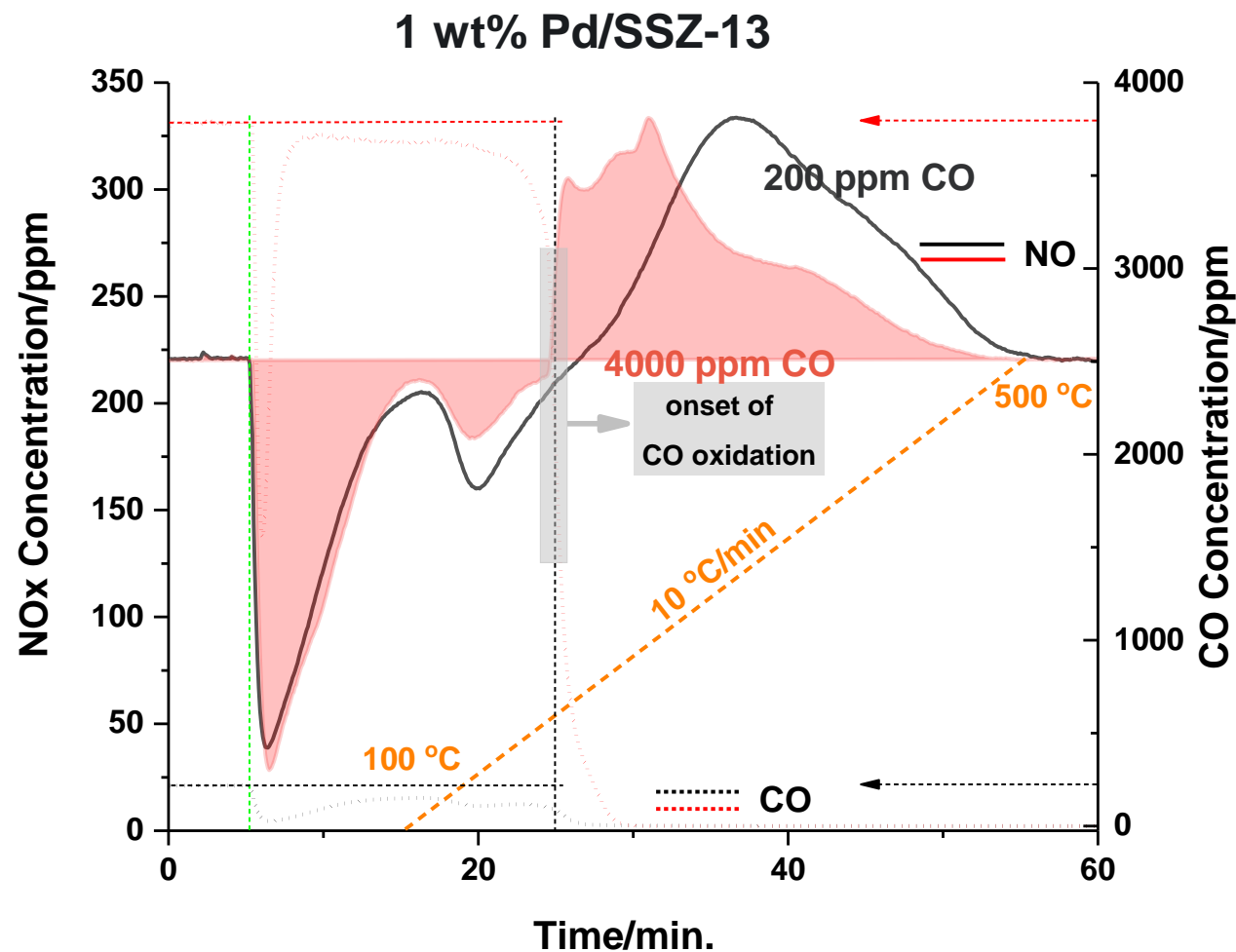


SSZ-13



- ▶ Our previous work showed that Pd/SSZ-13 is an efficient PNA material but has
 - Insufficient high temperature hydrothermal stability (performance degradation at $T > 750$ °C).
- ▶ Both Pd/FER and Pd/SSZ-39 address the major limitation of Pd/SSZ-13 with both high PNA performance *and* superior high temperature hydrothermal stability.
- ▶ Focus on the studies of the effects of high CO concentration *and* repeated cycles on NO_x uptake/release.

The Presence of CO in High Concentration (4000 ppm) Dramatically Alters the NO_x Release Profile on Pd/SSZ-13

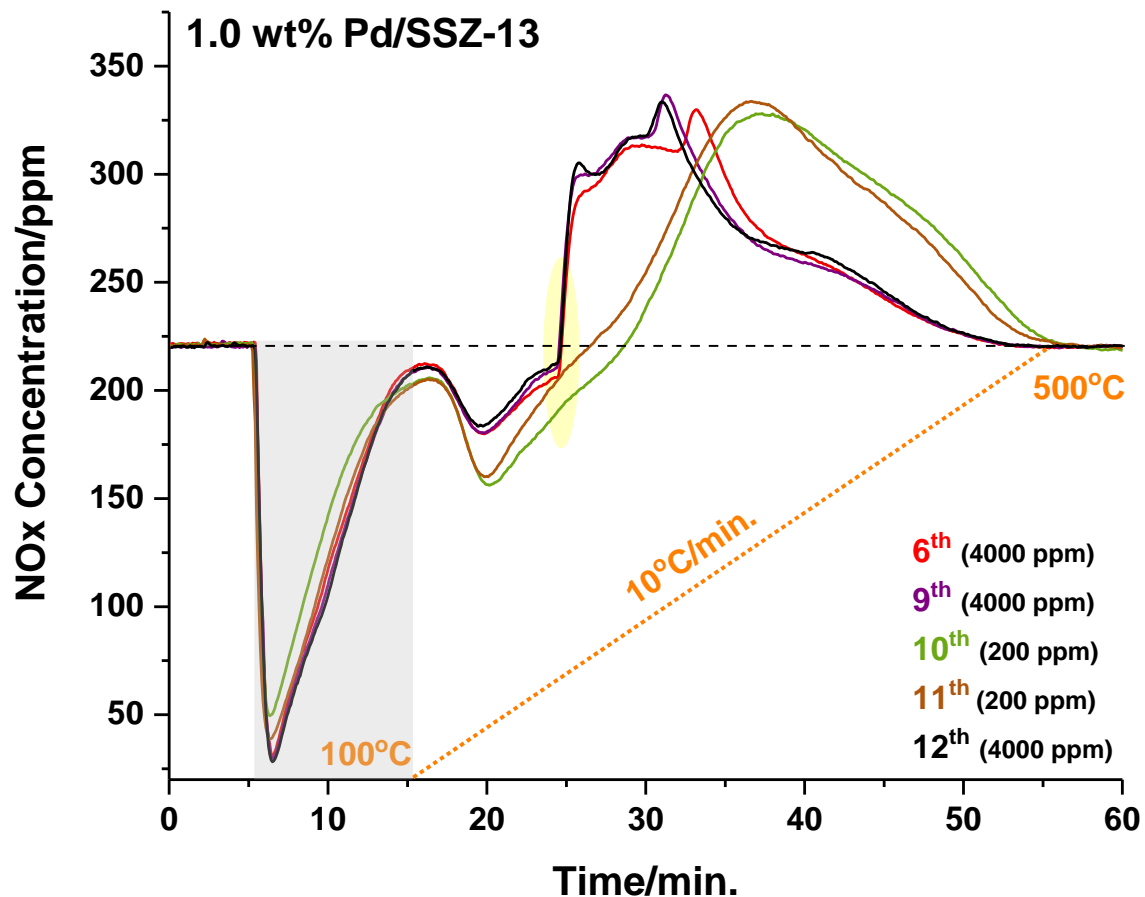


220 ppm NO_x (200 ppm NO and 20 ppm NO₂), 200/4000 ppm CO, 14% O₂, 3 % H₂O, balanced with N₂ at a flow rate of 300 sccm

- ▶ CO in low concentration (200 ppm) has no effect on either NO_x uptake or release.
- ▶ High concentration of CO (4000 ppm) dramatically changes the NO_x release profile, while it has no effect on the amount of NO_x uptake:
 - The sudden NO_x release in the presence of CO in high concentration (4000 ppm) coincides with the onset of CO oxidation.
 - The heat produced in CO oxidation seems to be responsible for the lower NO release temperature at high CO concentrations.

Technical Accomplishments: Pd/CHA

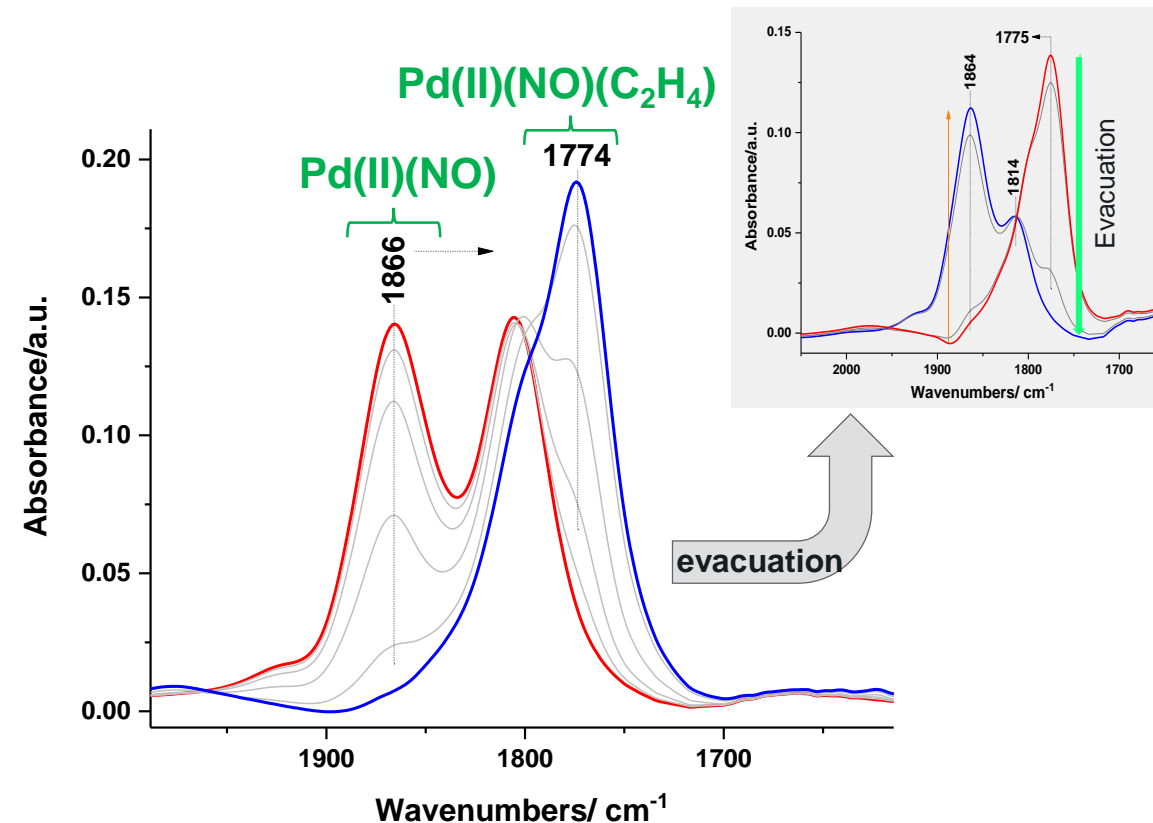
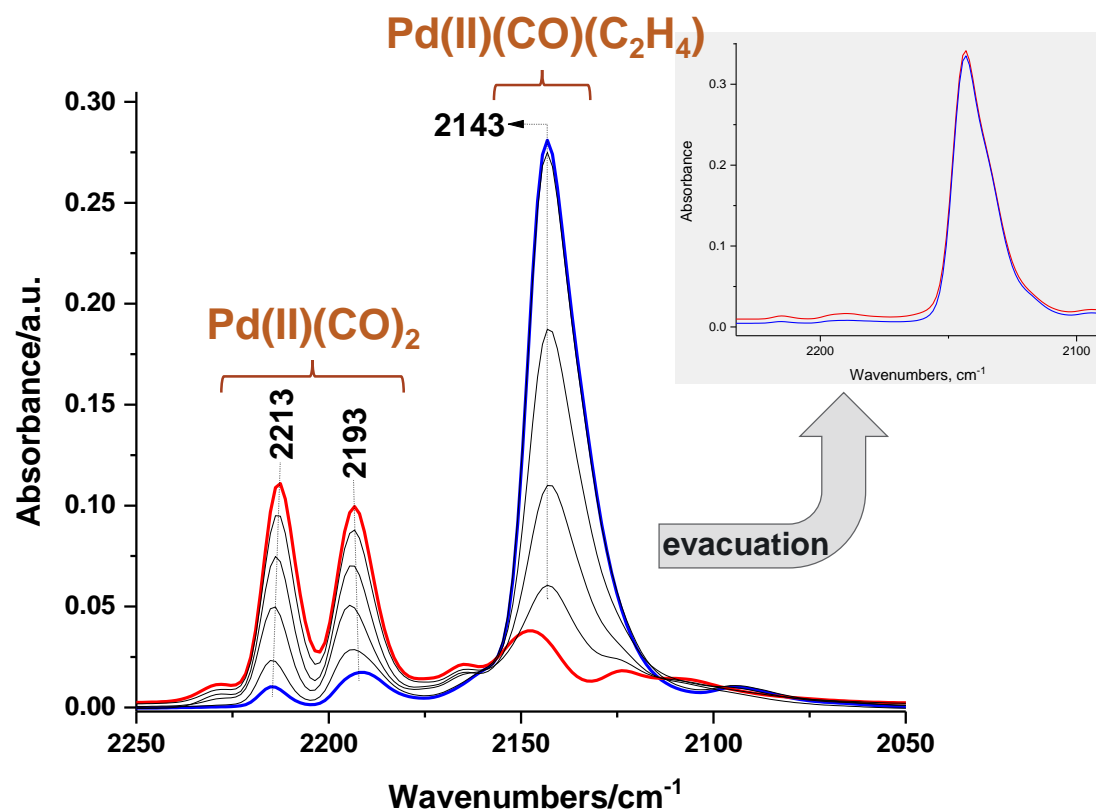
Excellent Cyclic Stability at up to 500 °C



220 ppm NO_x (200 ppm NO and 20 ppm NO₂), 200/4000 ppm CO,
14% O₂, 3 % H₂O, balanced with N₂ at a flow rate of 300 sccm

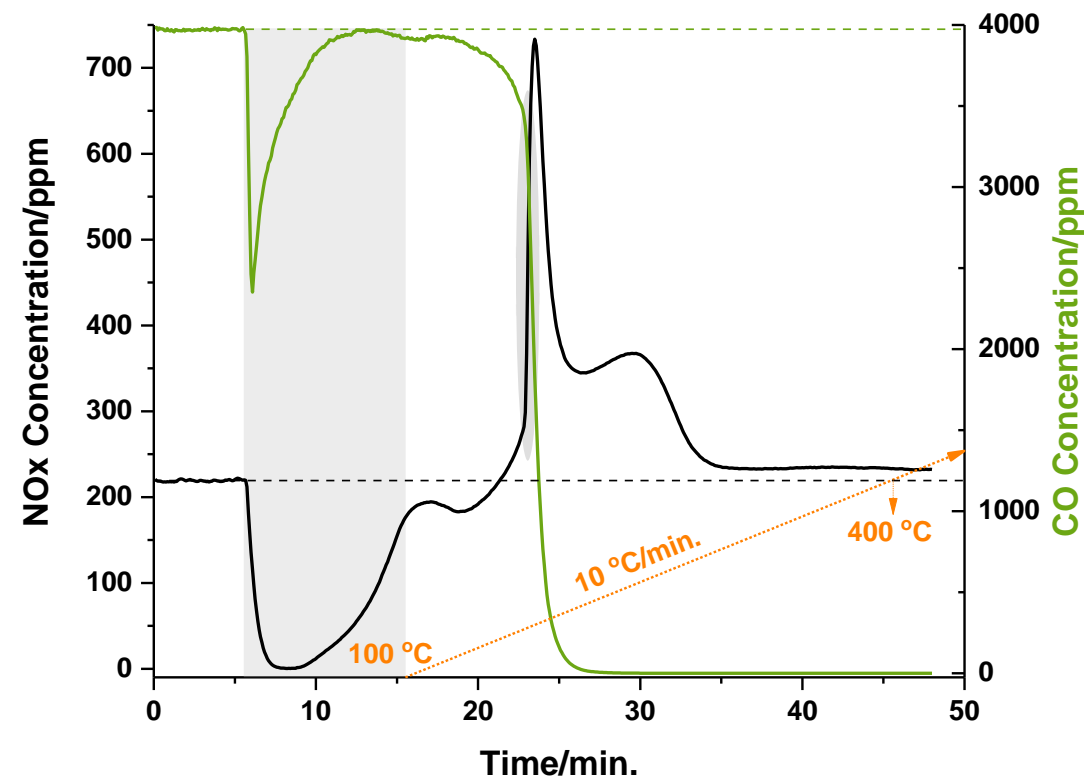
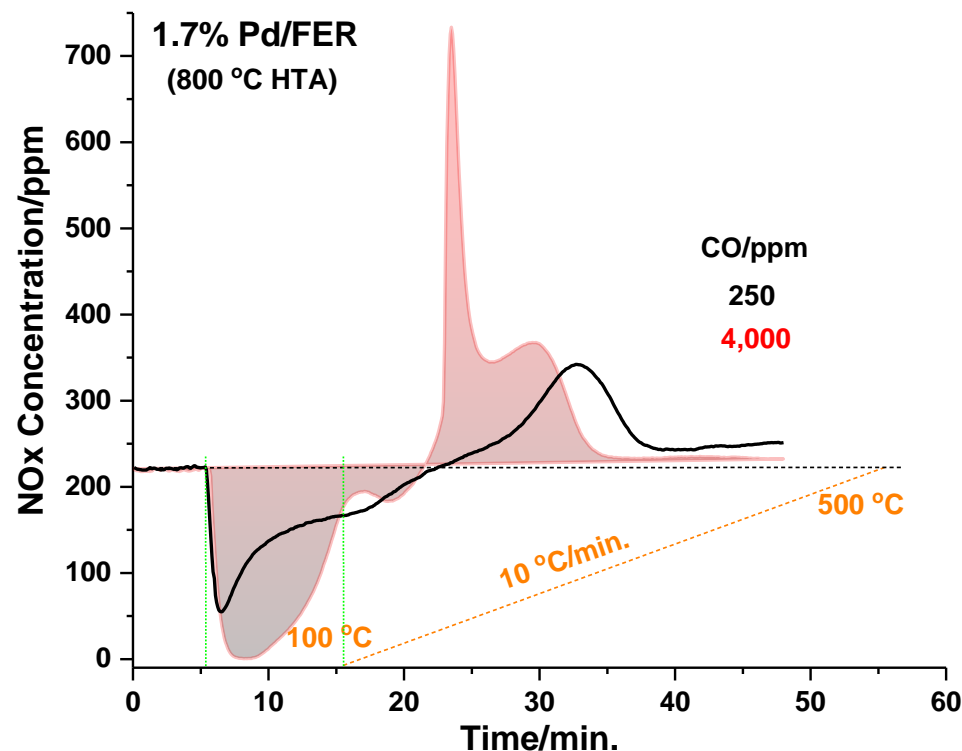
- ▶ Cycling NO_x release/uptake at low and high CO concentrations does not affect the adsorbed and released amount of NO_x.
- ▶ Cycling to 500 °C in the presence of CO in high amounts (4000 ppm) shifts the sudden NO_x uptake to the same lower temperature.
- ▶ The NO_x release profile in the presence of high amount of CO (4000 ppm) exhibits a characteristic “triplet” shape,
 - understanding of the structure of the release feature is part of future spectroscopy studies.

Presence of C_2H_4 May Adversely Affect NO_x Uptake by Forming Stable Mixed $(CO)(C_2H_4)$ Complex on $Pd(II)$ Sites



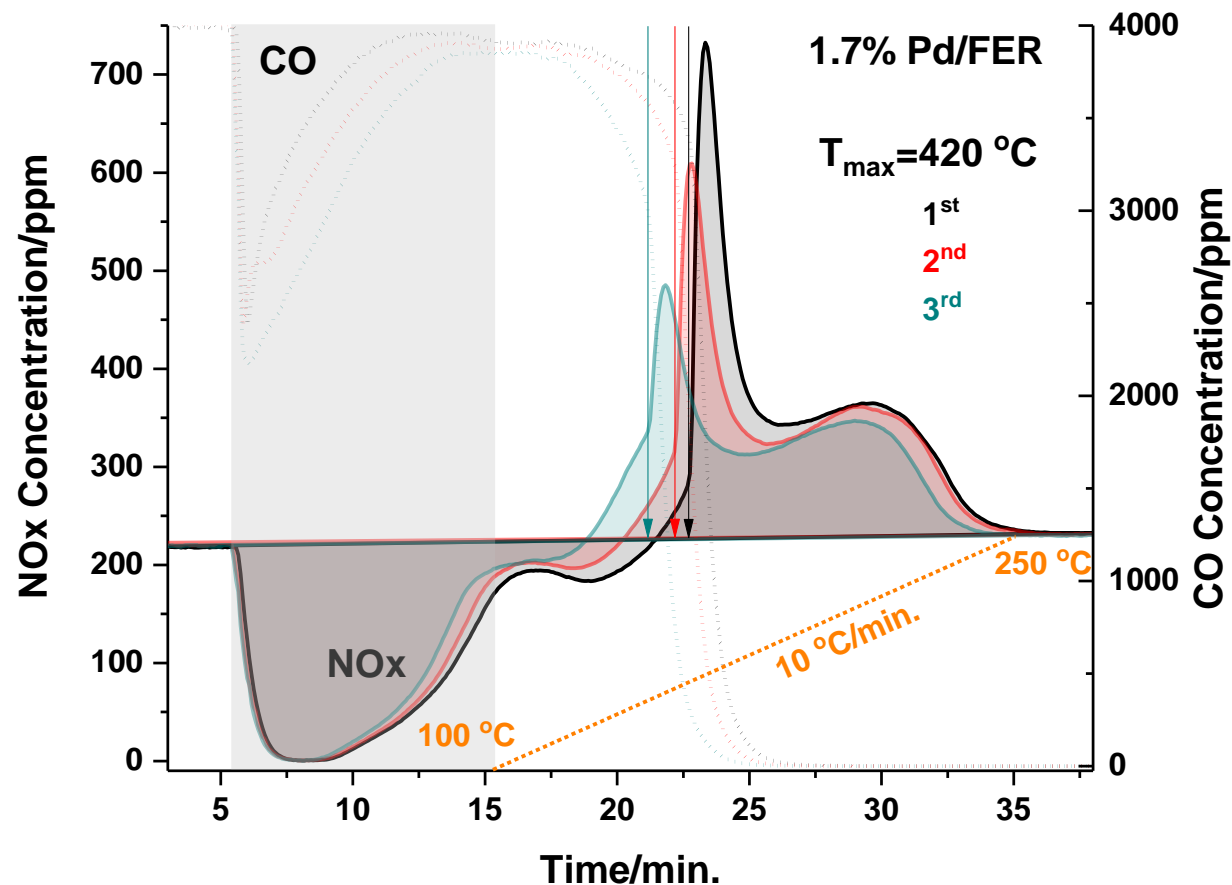
- ▶ C_2H_4 strongly interacts with the $Pd(II)(CO)_2$, forming a mixed ligand $Pd(II)(CO)(C_2H_4)$ complex which is very stable.
- ▶ $Pd(II)(NO)$ interacts with C_2H_4 and forms the $Pd(II)(NO)(C_2H_4)$ mixed-ligand complex, which is not stable under evacuation and readily loses C_2H_4 to regenerate the $Pd(II)(NO)$ complex.
- ▶ The $Pd(II)(OH)(NO)$ complex does not form ethylene complex.
- ▶ The high stability of the $Pd(II)(CO)(C_2H_4)$ complex may be detrimental to the NO_x uptake of Pd/SSZ-13 (future studies).

Both the Amount of NO_x Uptake/Release *and* the NO_x Release Temperature Vary with CO Concentration



- ▶ The release temperature of NO_x is lower on Pd/FER (~260 °C) than on Pd/CHA (~350 °C).
- ▶ In the presence of low amount of CO during NO_x uptake the amount of NO_x stored is lower on Pd/FER (NO/Pd~0.5) than on Pd/CHA (NO/Pd~1).
- ▶ The NO_x uptake increases significantly at high CO concentration (4000 ppm). Complete NO_x uptake occurs for ~2 min. [CO is needed to “position” Pd ions for NO_x uptake (supported by CO FTIR studies.)]
- ▶ Both NO_x release temperature and release profile change in the presence of large amount of CO.
- ▶ Similarly to Pd/CHA the sudden release of NO_x in the presence of CO in high concentration coincides with the onset of CO oxidation.

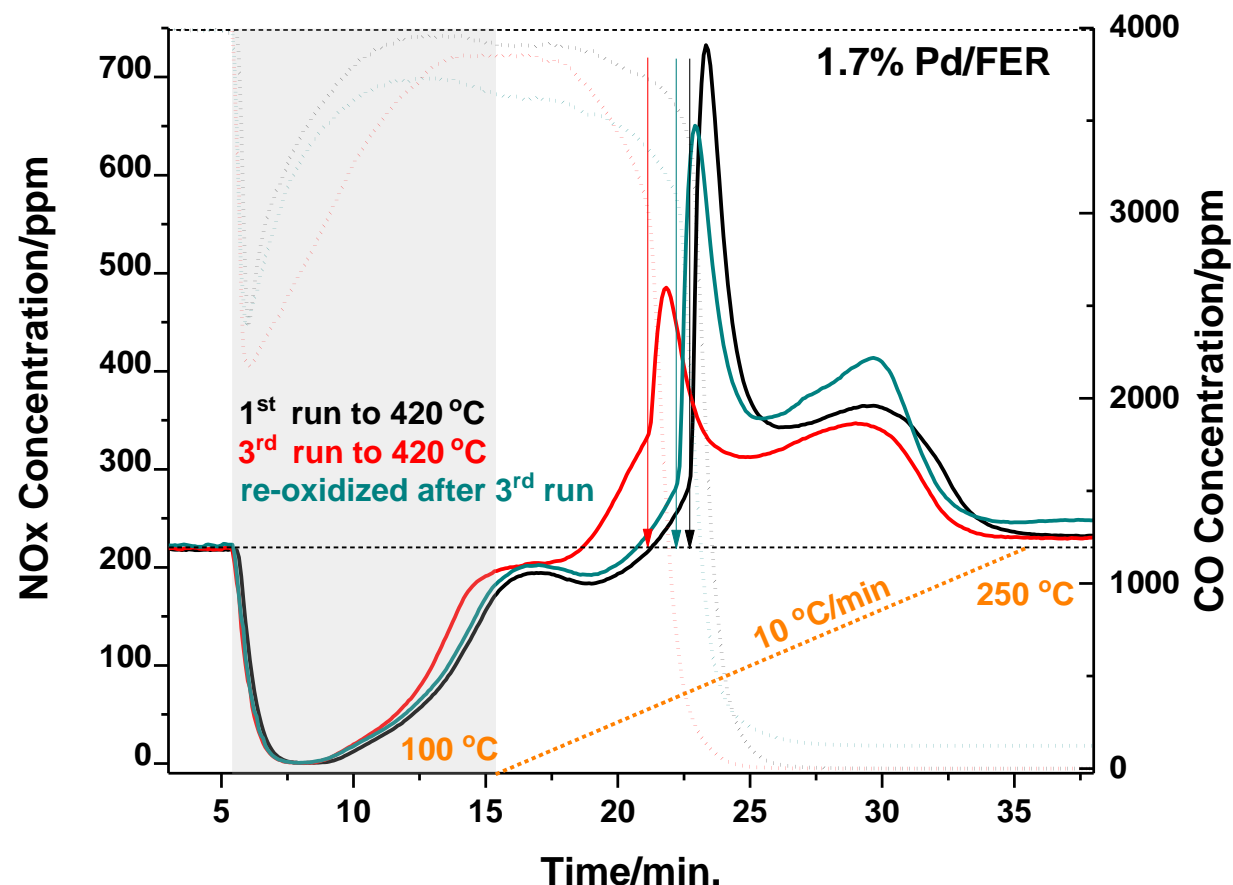
High Concentration of CO Gradually Shifts the Low Temperature NOx Release Profile in Repeated Cycles to 420 °C



- ▶ Low temperature NOx release peak shifts to lower values with each cycle, while the high temperature one is unchanged.
- ▶ The onset temperature for CO oxidation shifts to lower values in each consecutive NOx uptake/release cycle,
 - metallic Pd seems to form when the release cycle is run to $T < 450\text{ }^{\circ}\text{C}$.
- ▶ Total amount of NOx uptake slightly decreases with the number of cycles, (loss of Pd(II) adsorption sites as Pd(0) clusters form).

220 ppm NOx (200 ppm NO and 20 ppm NO₂), 4000 ppm CO, 14% O₂, 3% H₂O, balanced with N₂ at a flow rate of 300 sccm (after the completion of each NOx uptake/release the system is purged at 420 °C with air for 2 hrs prior to cooling it to 100 °C for the next NOx uptake cycle)

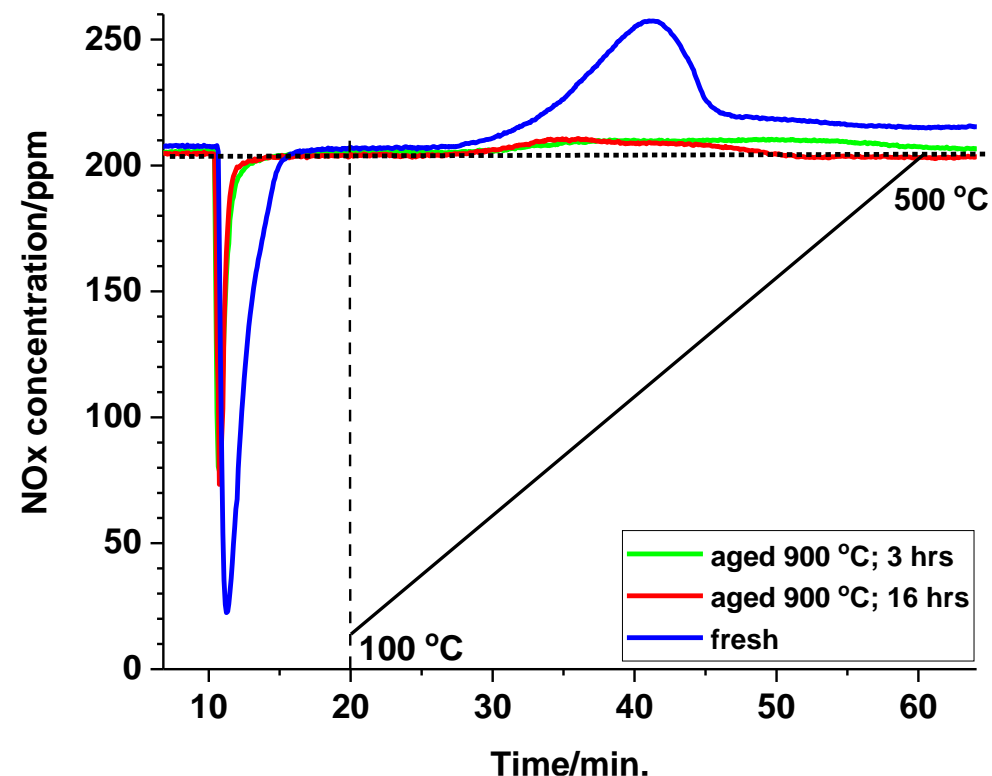
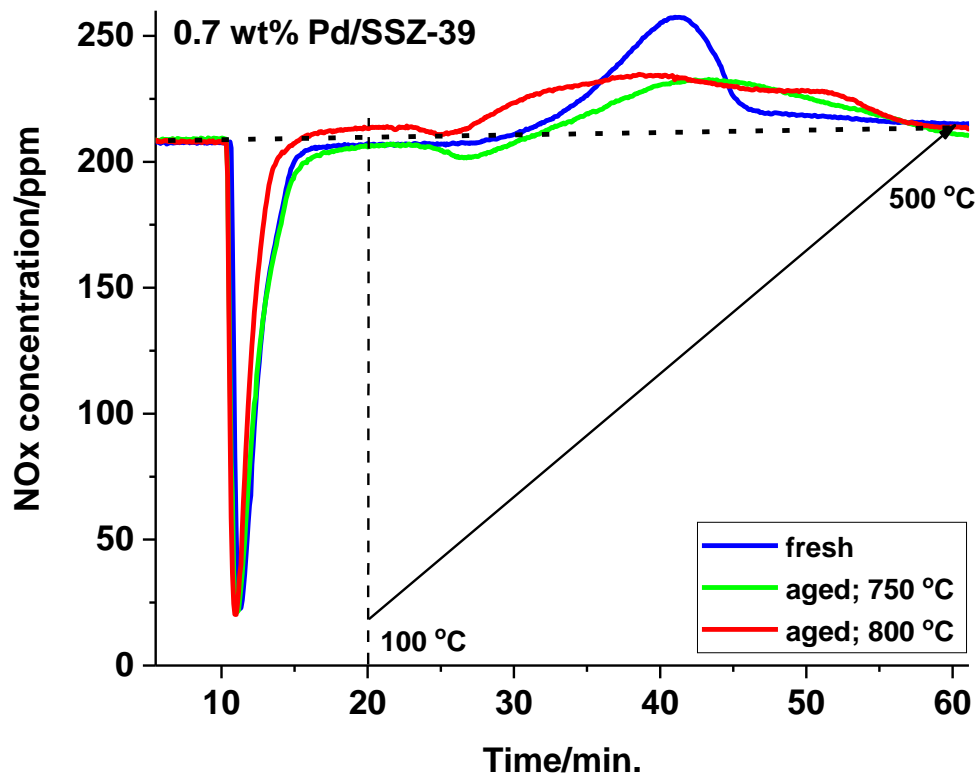
Technical Accomplishments: Pd/FeR NO_x Uptake/Release is Completely Regenerated (after cycles to 420 °C) by Calcination at 720 °C



220 ppm NO_x (200 ppm NO and 20 ppm NO₂), 4000 ppm CO, 14% O₂, 3% H₂O, balanced with N₂ at a flow rate of 300 sccm (after the completion of each (1,2,3) NO_x uptake/release cycle the system is purged at 420 °C with air for 2 hrs prior to cooling it to 100 °C for the next NO_x uptake cycle; after the 3rd run the sample is heated to 720 °C in air for 30 min.)

- ▶ After high temperature calcination the NO_x uptake completely recovers to its original value (from NO/Pd~0.7 to NO/Pd~1). (~2 min of complete NO_x uptake at 100 °C)
- ▶ The low temperature NO_x desorption feature shifts back to higher temperature, very close to the initial one.
- ▶ The onset temperature of CO oxidation shifts to higher temperature, close to the initial value.
- ▶ Pd(0) clusters re-disperse during high temperature (720 °C) calcination.
- ▶ Both NO and H₂O are seen to desorb (~550 and ~600 °C, resp.) during calcination to 720 °C.

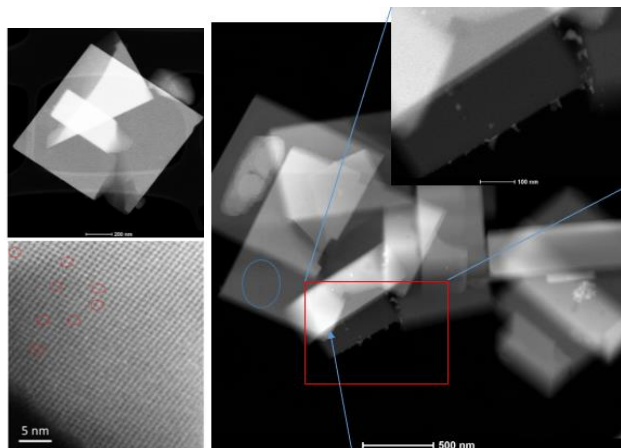
Similar NO_x Uptake/Release Performance to Pd/SSZ-13, but much Better High Temperature Hydrothermal Stability



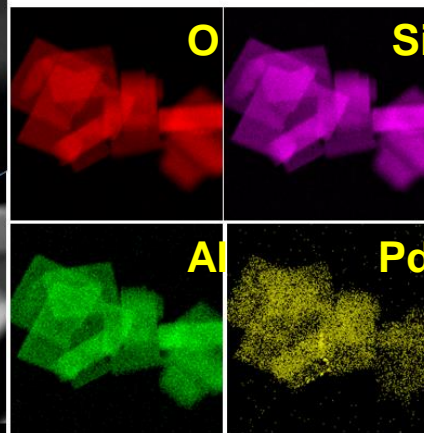
- ▶ NO/Pd in the fresh adsorber is ~0.9, suggesting high Pd dispersion.
- ▶ High T hydrothermal aging up to ~800 °C does not degrade NO_x storage capacity.
- ▶ Similarly to Pd/SSZ-13 the shape of the NO_x release profile changes with high T hydrothermal aging.
- ▶ High T hydrothermal aging at and above 900 °C results in a dramatic decrease in NO_x uptake.

Extreme High Temperature Hydrothermal Stability of SSZ-39 Framework is Observed

HAADF-STEM

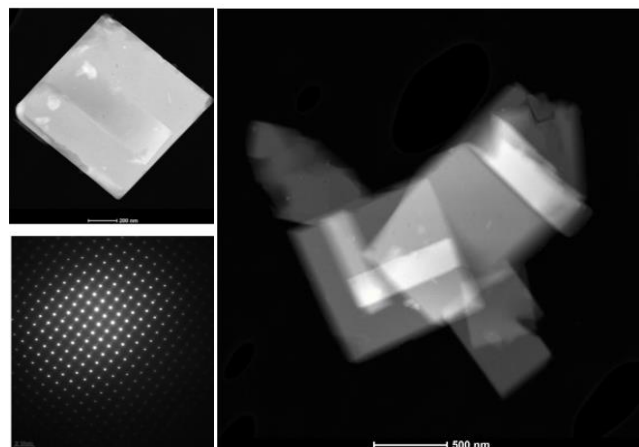


EDS

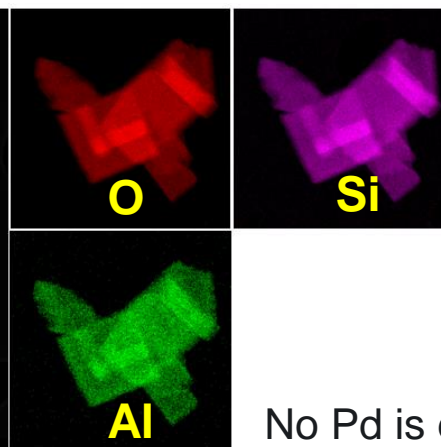


Fresh sample (500 °C calcined)

HAADF-STEM

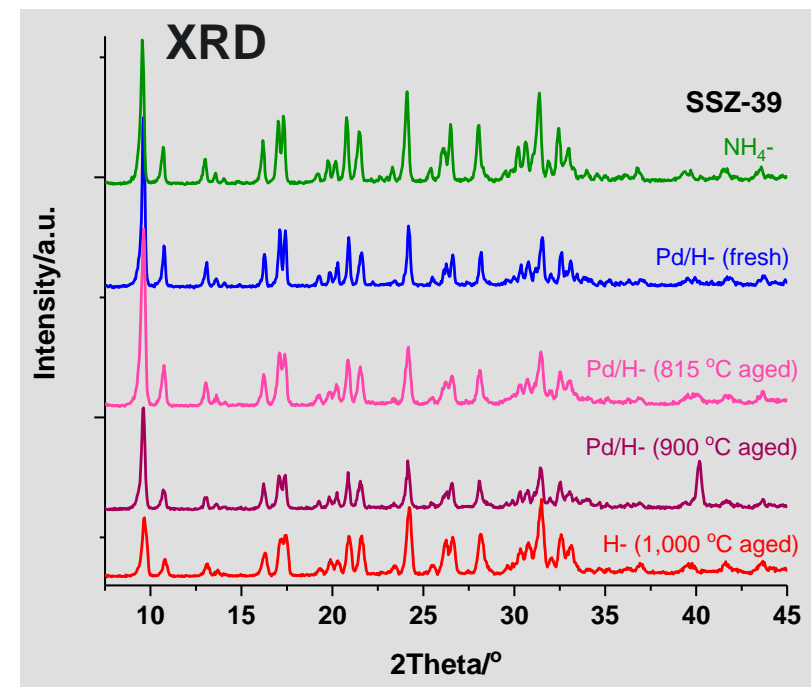


EDS



Hydrothermally aged sample at 900 °C

After calcination at 500 °C uniform Pd dispersion is observed over the zeolite crystallites.

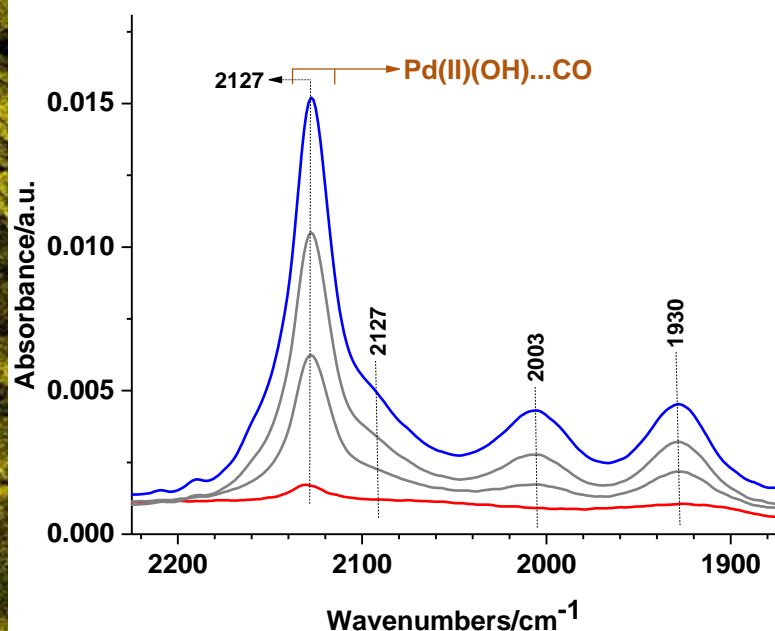


Crystallinity is mostly preserved even after hydrothermal aging at 900 °C.

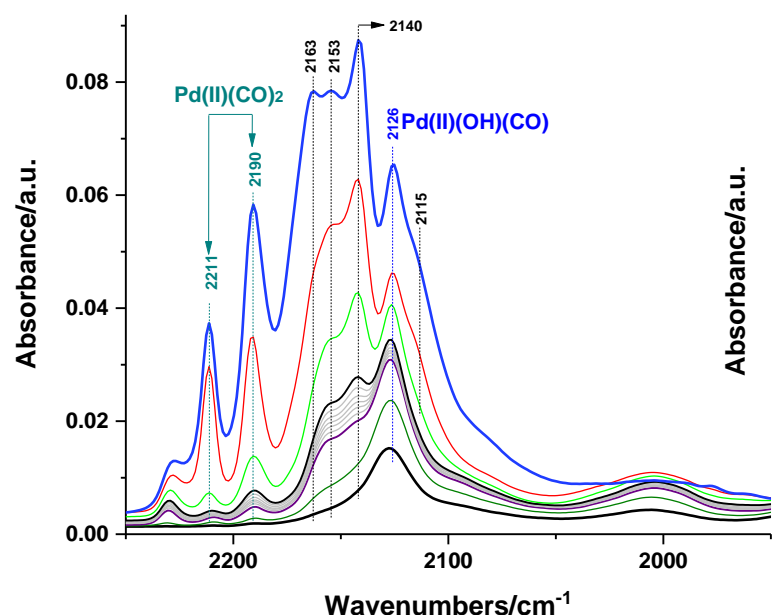
No Pd is detected after hydrothermal aging at 900 °C.

FTIR Spectra after CO and NO Adsorption Reveals Multiple Adsorption Sites

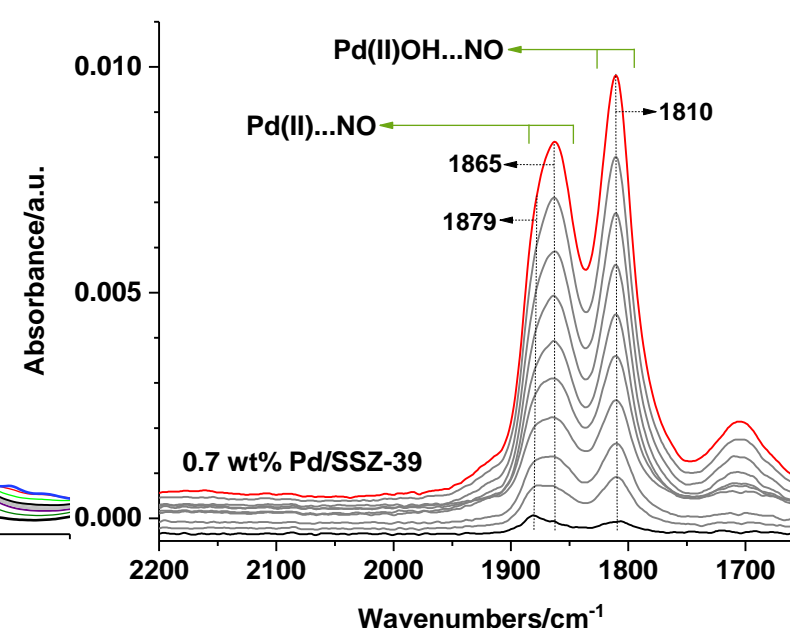
Low CO pressure
($P_{\text{CO (max)}} < 0.1$ Torr)



High CO pressure
($P_{\text{CO (max)}} \sim 10$ Torr)



NO adsorption
($P_{\text{NO(max)}} \sim 0.5$ Torr)



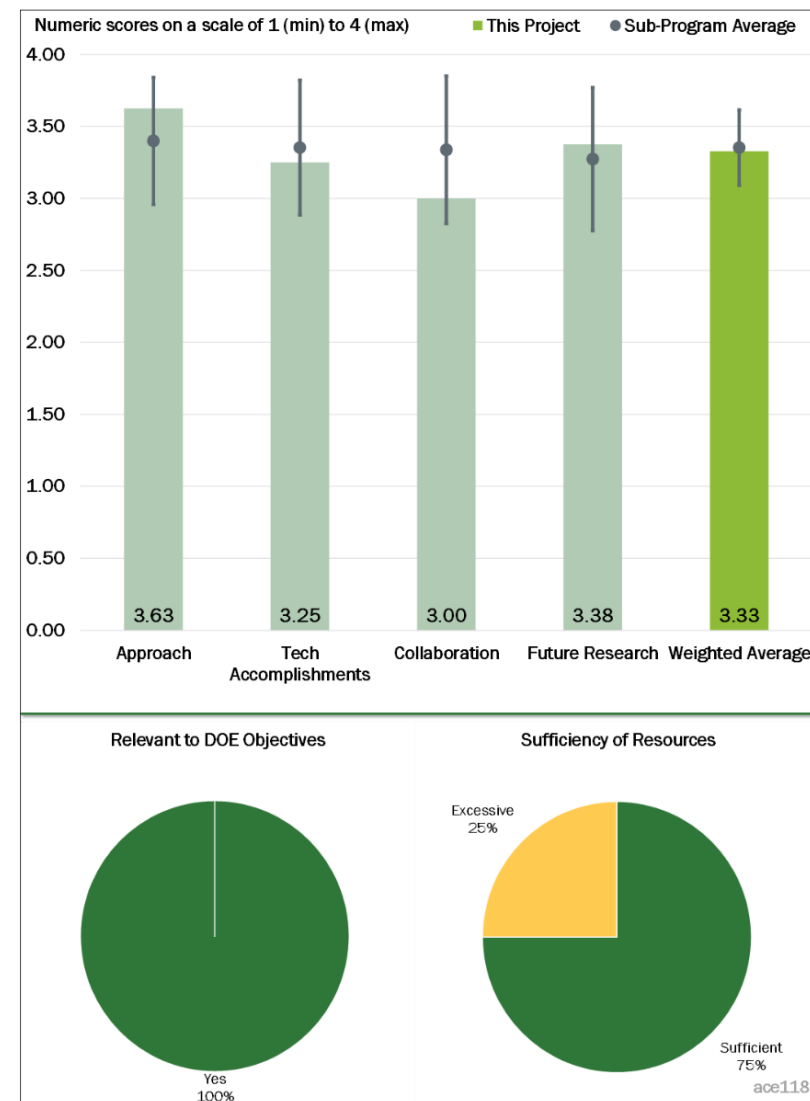
- ▶ At low P_{CO} , Pd(II)(OH)...CO complexes form (very small amount of Pd(0)...CO also forms).
- ▶ At higher CO pressures, Pd(II)...CO, Pd(II)...(CO)₂ and even Pd(II)...(CO)₃ complexes form.
- ▶ NO adsorbs on both Pd(II) and Pd(II)OH sites.
- ▶ **The adsorption sites available for CO and NO adsorption in Pd/SSZ-39 are less uniform than in Pd/SSZ-13.** (NO and CO co-adsorption data are shown in the Technical Backup Slides.)

Responses to Previous Years Reviewers' Comments

- ▶ Nearly all the comments from the reviewers last year were very supportive and complimentary, especially regarding our approach and technical accomplishments.
- ▶ Some comments/recommendations included:
 1. The research presented felt too fundamental (“felt like BES rather than EERE”).
 2. “it appeared to the reviewer that ORNL is developing a similar technology. ... might be an opportunity to co-develop this technology to ... maximize resources.”
 3. Lack of collaboration.
 4. “urgency of investigating the loss of NOx storage efficiency on repeated cold-start tests”

PNNL response

1. Fundamental studies (i.e., understanding structure/function relationships) are vital to the development of viable kinetic models. [Fundamental studies on emission control catalysis is too close to practical applications for BES to consider funding it.]
2. We have provided our best performing Pd/SSZ-13 PNA samples to ORNL for cross examination.
3. We have very close collaboration and communication (e.g., monthly teleconfs) with BASF to address the key issues of industrial importance.
4. One of the main focus areas for the past year was repeated cold-start test with varied CO levels.



Collaboration and Coordination with other Institutions

Collaborators/Coordination

- ▶ Oak Ridge National Lab: Melanie Debusk, Jim Parks, Josh Pihl, Vitaly Prikhodko, Todd Toops
(sample exchange for performance cross check)
- ▶ BASF: Saeed Alerasool, Pascaline Tran, Xinyi Wei, Jeff Hoke
(monthly discussion; sample exchange)
- ▶ Sofia University, Bulgaria: Hristiyan A. Aleksandrov, Iskra Koleva and Georgi N.Vayssilov
(DFT calculations: adsorbate binding, reaction mechanisms, spectra interpretation)

Acknowledgements

- ▶ DOE EERE Vehicle Technologies Program: Gurpreet Singh, Ken Howden and Siddiq Khan.

Remaining Challenges and Barriers

- ▶ Performances under extreme conditions including temperatures, exhaust gas compositions such as reducing conditions in the presence of hydrocarbons.
- ▶ Activation of Pd/FER under high CO concentrations and the re-activation after multiple uptake/release cycles.
- ▶ Interference with other catalysts such as DOC.

Proposed Future Work

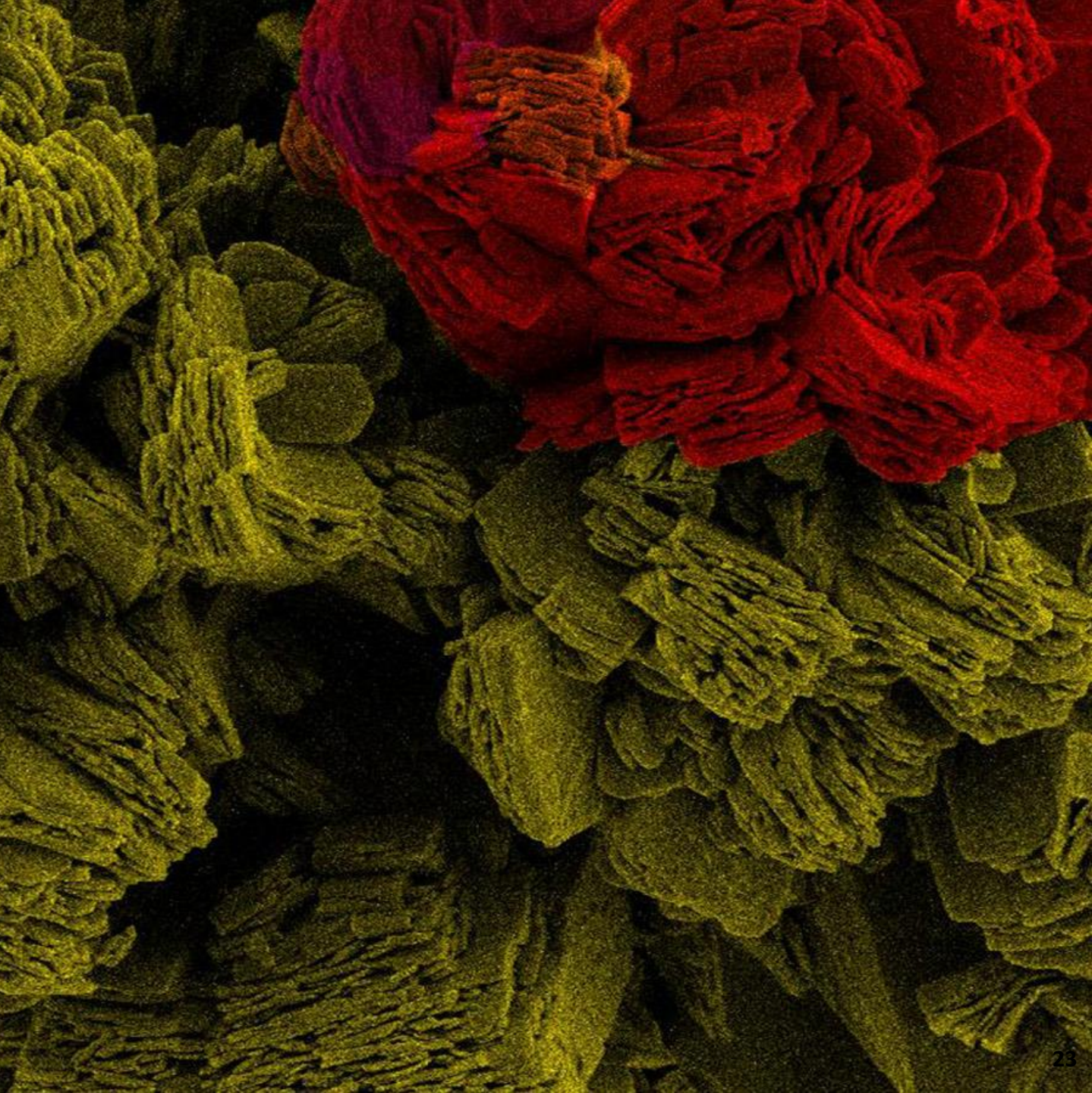
- ▶ Evaluate PNA performances of Pd/CHA under conditions of high HC (and CO) concentration, understand the mechanisms of PNA degradation, and provide guidance in mitigating the issue.
- ▶ Understand the activation, deactivation and regeneration of Pd/FER under different NO_x uptake/release conditions (i.e., low and high CO (and HC) concentrations).
- ▶ Study the poisoning mechanisms of PNA materials by non-sulfur compounds and HC.
- ▶ Understand the potential interference and interactions with DOC etc.

Any proposed future work is subject to change based on funding levels

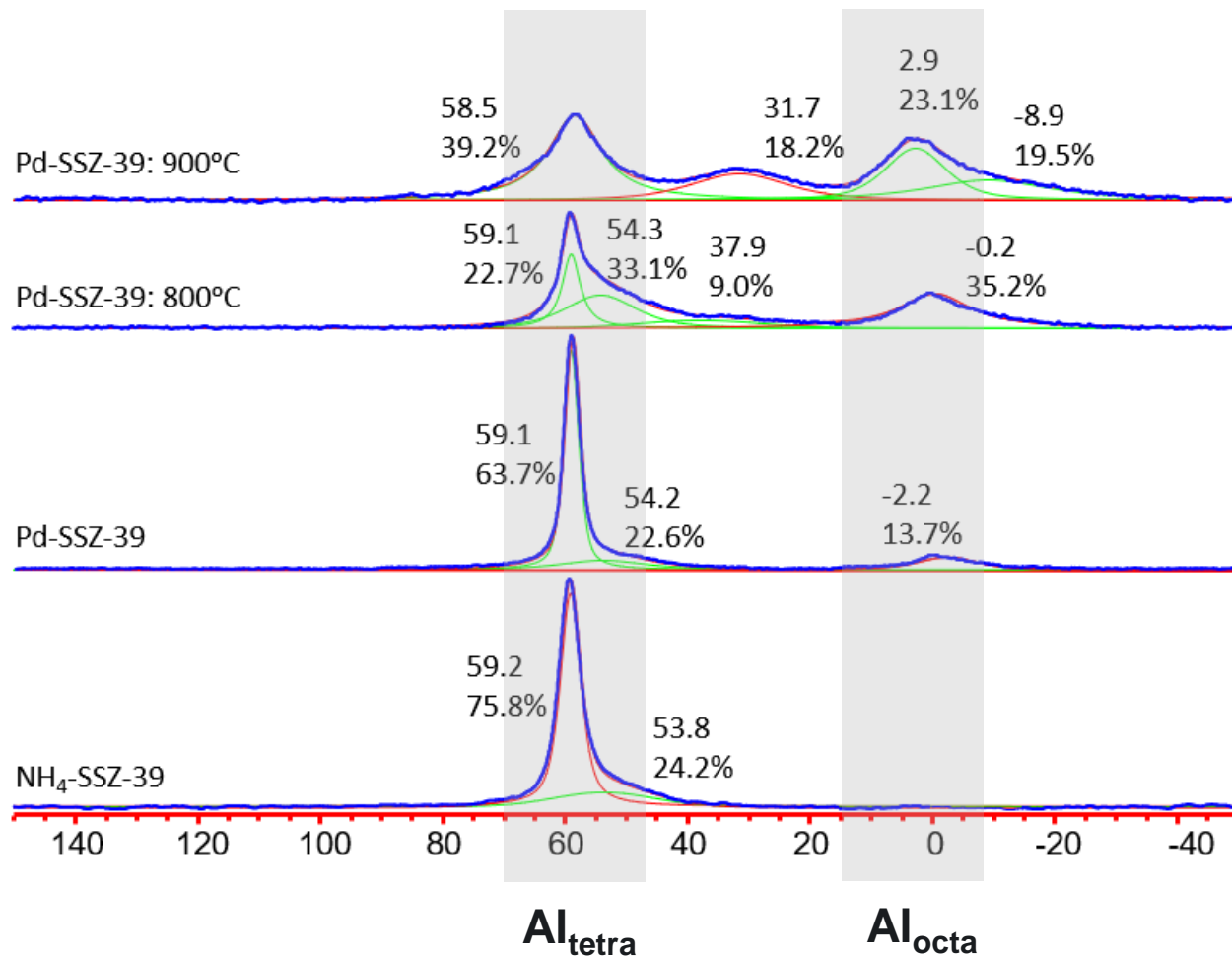
Summary

- ▶ Demonstrated excellent NO_x uptake/release properties for three small pore, Pd loaded zeolites.
- ▶ Showed that mixed (CO)(C₂H₄) and (NO)(C₂H₄) complexes can form on the Pd(II) sites that may negatively affect NO_x uptake properties. [(CO)(C₂H₄) complex in Pd/SSZ-13 is very stable.]
- ▶ Demonstrated superior high temperature hydrothermal stability for both the SSZ-39 and FER.
(Pd/FER operates efficiently only in the presence of CO in high concentrations.)
- ▶ Understood the substantial influences of high CO concentration on the NO_x uptake/release properties of zeolite-based PNAs:
 - Enhances NO_x uptake
 - Dramatically lowers the temperature of NO_x release.
- ▶ Understood the performance loss of Pd/FER during repeated low temperature NO_x uptake/release cycling.
- ▶ Demonstrated full regeneration of Pd/FER after low temperature cycling by high temperature calcination.
- ▶ Showed that Pd/SSZ-39 PNA deactivates at T>900 °C due to Pd removal, and not by the collapse of the zeolite framework.

Technical Backup Slides

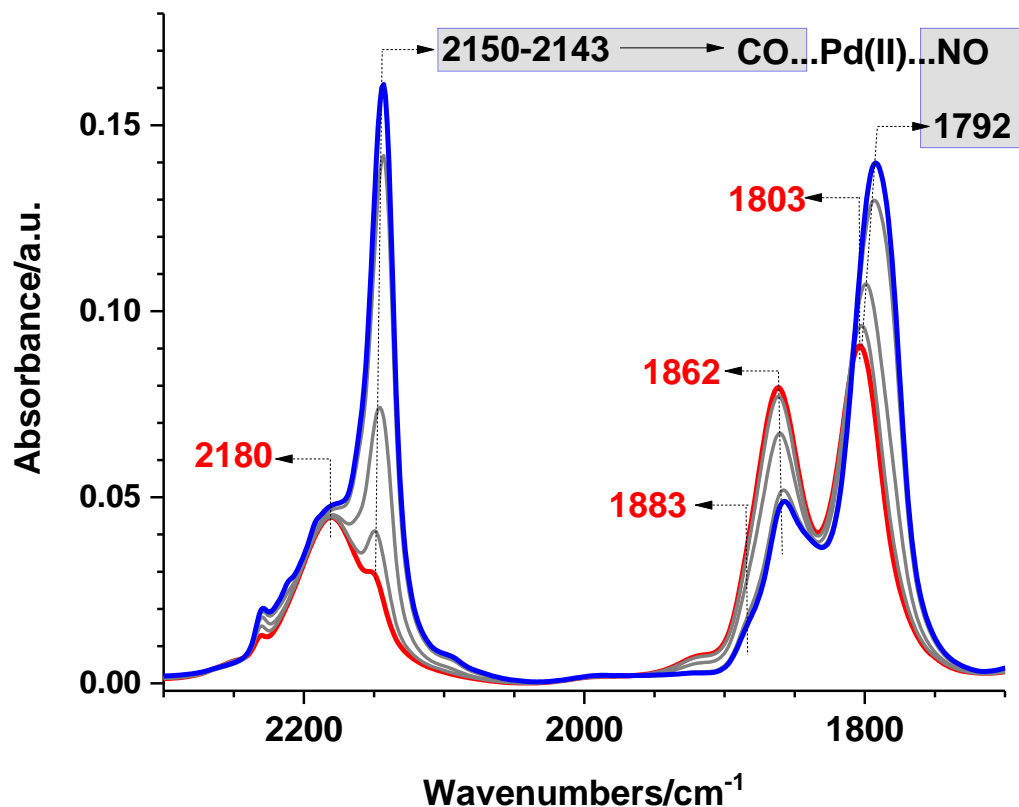


Pd/SSZ-39: ^{27}Al MAS NMR Spectra Confirm that most of the Al Stays in Tetrahedral Coordination even after 900 °C HTA



- ▶ SSZ-39 structure is thermally stable to at least 900 °C under hydrothermal aging.
- ▶ Performance loss must be related to loss of Pd adsorption sites at $T > 850$ °C.

Pd/SSZ-39: Exposure of the NO_{ads}/Pd/SSZ-39 to CO Results in the Formation of Mixed CO...Pd(II)...NO Complexes



- ▶ CO can adsorb on the Pd(II)...NO species to form mixed CO...Pd(II)...NO complexes.
- ▶ Pd(II)(OH) ... NO species do not interact with CO.
- ▶ Evacuation of the system restores the initial spectrum recorded after NO adsorption.